Organometallic intermediates in the synthesis of graphene nanoribbons on Ag(111)

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We investigate bottom-up growth of N = 7 armchair graphene nanoribbons (7-AGNRs) from the 10,10'-dibromo-9,9'-bianthracene (DBBA) molecules on the Ag(111) substrate with the focus on the role of organometallic (OM) intermediates [1]. It is demonstrated that DBBA molecules on Ag(111) are partially (half) debrominated at room temperature and lose all bromine atoms at elevated temperatures. Similar to DBBA on the Cu(111) substrate, debrominated molecules form OM chains on Ag(111). However, the formation of polyanthracene chains from OM intermediates *via* an Ullmann-type reaction is feasible on Ag(111), in contrast to the case of Cu(111). A cleavage of the C – Ag bonds on Ag(111) occurs at temperatures below the thermal threshold for surface-catalyzed dehydrogenation, while on Cu(111) the cleavage of the C – H and the C – Cu bonds occurs in the same temperature window. Consequently, while OM intermediates obstruct the Ullmann reaction between DBBA molecules on the Cu(111) substrate, they are not an obstacle for the formation of polyanthracene chains on Ag(111). If the Ullmann-type reaction on Ag(111) is inhibited, heating of the OM chains produces nanographenes instead. Heating of the polyanthracene chains produces 7-AGNRs, while heating of nanographenes causes the formation of disordered structures with the possible admixture of short GNRs.

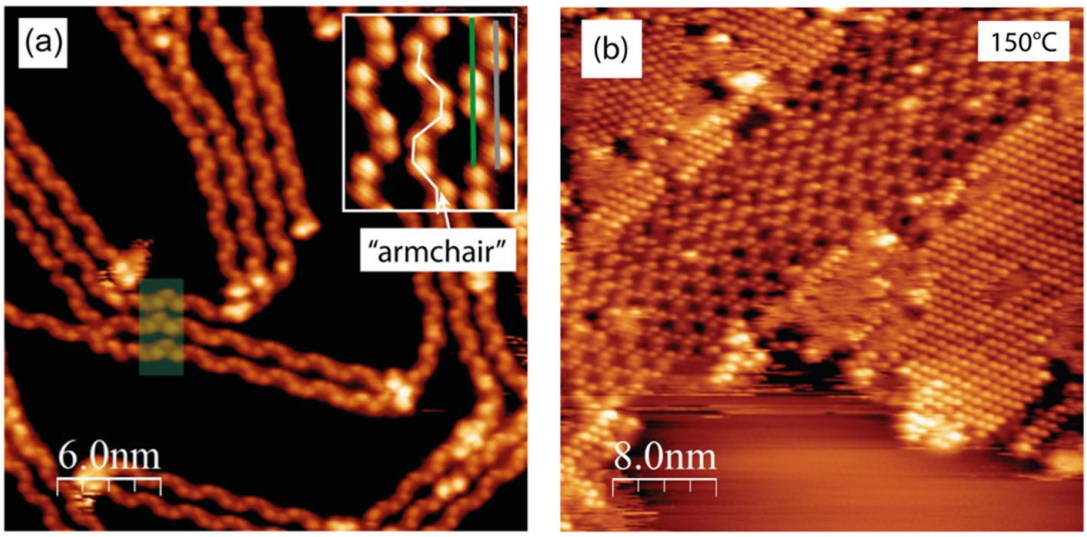

Figure: (a) OM chains grown by annealing DBBA/Ag(111) at 120°C. Inset: three OM chains with "armchair" chain pattern. (b) Transformation of OM chains to covalent chains at 150°C.

[1] K. A. Simonov et al., Scientific Reports **8**, 3506 (2018), doi:10.1038/s41598-018-21704-3.